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AN IMPROVED CLOSURE OF THE BORN-GREEN-YVON EQUATION FOR 1/1
THE ELECTRIC DOUBLE LAYER(U) PUERTO RICO UNIV RIO

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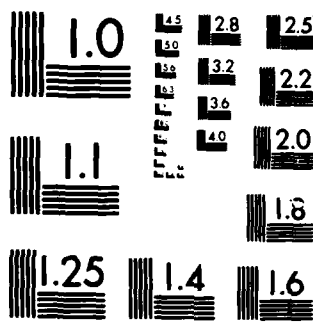
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In particular ~~we are able to go to~~ higher densities than those hitherto published in the literature. For low density 2-2 and 2-1 electrolytes the agreement is not as good as for the other theories. *Fig. 2.11.9*

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TECHNICAL REPORT #20

AN IMPROVED CLOSURE OF THE BORN-GREEN-YVON EQUATION FOR THE
ELECTRIC DOUBLE LAYER

by

C. Caccamo , G. Pizzimenti and L. Blum⁺
Department of Physics
University of Puerto Rico
Rio Piedras, PR 00931

Istituto di fisica teorica
Università di Messina
Messina, Italy

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Abstract.

An extensive series of calculations are made to compare an improved closure of the Born-Green-Yvon (BGY) equation for the electric double layer of primitive electrolytes to existing Monte Carlo simulation and other theories, such as the Modified Poisson-Boltzmann (version 5) (MPB5) and the Hypernetted Chain/Mean Spherical Approximation (HNC/MSA), and its recent improvements.

In contrast to these theories the BGY equation satisfies the contact theorem always. Furthermore the bulk pair correlation functions used are the most accurate available, namely the HNC bulk results.

The results show very good general agreement to the computer work for high densities and surface charges. In particular we are able to go to higher densities than those hitherto published in the literature. For low density 2-2 and 2-1 electrolytes the agreement is not as good as for the other theories.

Introduction.

The primitive model of the electrode interface consists of a perfectly smooth surface, which represents the metal, and a collection of charged hard spheres representing the ions. All of it is immersed in a dielectric continuum.

Clearly this model is not an accurate representation of the real electrode-electrolyte interface, but it can be simulated in computers, and therefore it is possible to assess the accuracy of approximation schemes for it.

The early experimental work has used the theories of Gouy⁽¹⁾, Chapman⁽²⁾ and Stern⁽³⁾ with reasonable success, in spite of the fact that these theories neglect completely the excluded size effects and correlation effects between the ions. Recently, various theories have been proposed to include these correlations in the treatment.⁽⁴⁻¹⁰⁾

One of the primary goals of this exercise is to develop an equation capable of handling very dense and highly coupled systems, such as the molten salts and the non-primitive electrolyte (mixture of hard ions and dipoles) against a metal electrode.

In this regime it is most important that the contact relation^(11,12)

$$k_B T \sum_i q_i(0) = P_B + \epsilon E_0^2 / 8\pi \quad (1)$$

be exactly satisfied. In (1) $k_B T$ is the Boltzmann thermal factor, P_B is the bulk pressure, ϵ is the dielectric constant ($\epsilon = 80$ for water in the primitive model, and $\epsilon = 1$ for the non-primitive case).

$q_i(0)$ is the contact density of species i (which could be either an ion or^a solvent molecule in the non-primitive case) and the summation is over all the species; E_0 is the applied electric field.

- 1 -

All species are assumed to be hard spheres.

The BGY equation and any of its closures will always satisfy the contact relation. For this reason we have chosen this equation in this work^(9,10). In this paper we study and extend an improved ansatz for the closure of the BGY which we proposed earlier⁽¹³⁾. Here the pair correlation function is forced to satisfy the local electroneutrality condition^(9,14,15) and to be positive definite. We compare the results of this theory to the extensive work of Valleau and coworkers⁽¹⁶⁾ and Snook et al.⁽¹⁷⁾. We find that the agreement is excellent for the values of the contact potentials for the more concentrated solutions. The density and potential profiles are in general good agreement also.

With our method we have been able to get results for very concentrated solutions (up to 4 M of a 1-1 electrolyte). In these cases we observe a marked layering of solute against the electrode wall. For the dilute ionic solutions (0.05 M for the 2-2 and 2-1 electrolytes, 0.1 M for the 1-1 electrolytes) the results are in general inferior to the MPB5.

In Section 2 we describe our basic equations. In Section 3 we give the results for the 1-1, 2-2 and 2-1,1-2 electrolytes.

A brief discussion of the general conclusions is given at the end.

Sect. 2: Basic equations.

We consider a model in which the ions are hard spheres of diameter σ_i and number density ρ_i . The solvent is a continuum of dielectric constant ϵ , and the electrode is flat, smooth and has the same dielectric constant ϵ .

For this model we define the one and the two particle distribution functions

$$\rho_1(\vec{r}_1) = \rho_1(1) \quad (2),$$

$$\rho_{ij}(\vec{r}_1, \vec{r}_2) = \rho_{ij}(1,2) \quad (3),$$

where $\vec{r}_1 \equiv (x_1, y_1, z_1)$ is the position of particle 1, z_1 being its distance from the wall

The pair correlation function is defined by

$$\rho_{ij}(1,2) = \rho_1(1) \rho_j(2) g_{ij}(1,2) \quad (4)$$

and we also need

$$h_{ij}(1,2) \equiv g_{ij}(1,2) - 1 \quad (5).$$

These functions must satisfy the asymptotic conditions

$$\lim_{z \rightarrow \infty} \rho_1(1) = \rho_{1-} \quad (6),$$

$$g_{ij}(1,2) = g_{ij}^{\text{bulk}}(r_{12}) \quad (7),$$

$$h_{ij}(1,2) = h_{ij}^{\text{bulk}}(r_{12}) \quad (8),$$

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$. This means that all the correlations far away from the electrode must be equal to those of the homogeneous bulk.

Our basic approach is to write the Born-Green-Yvon equation as a modification of the Poisson-Boltzmann equation⁽¹⁰⁾.

Consider the first BGY⁽¹⁸⁾ equation

$$-k_B T \nabla_1 \ln \rho_1(1) = -e_1 E_0 + \int d\vec{r}_2 \sum_j \rho_j(2) g_{ij}(1,2) \nabla_1 U_{ij}(r_{12}) \quad (9)$$

for $z_1 > \sigma_1/2$

where the pair potential $U_{ij}(r_{12})$ has two contributions

$$U_{ij}(r_{12}) = U_{ij}^0(r_{12}) + e_i e_j / \epsilon r_{12} \quad (10),$$

where $U_{ij}^0(r_{12})$ is the short ranged part of the ion-ion interaction. We introduce the local electrostatic potential

$$\phi(1) = -E_0 z_1 + \int dr_2 \sum_j q_j(2) / \epsilon r_{12} \quad (11).$$

Adding and subtracting the gradient of the second term of (11) into (9), we eliminate the divergence of the right hand side of (11). Using also the relation

$$\nabla_1 U_{ij}^0(r_{12}) = -k_B T \delta(r_{12} - \sigma_{ij}) (z_{12}/r_{12}) \quad (12),$$

$$\text{where } \sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (13),$$

$$z_{12} = z_1 - z_2 \quad (14),$$

and $\delta(x)$ is the Dirac delta function, we get after some simple transformations:

$$\begin{aligned} -k_B T \nabla_1 \ln q_1(1) = & e_i \nabla_1 \phi(1) - k_B T \sum_j \int d\vec{r}_2 q_1(2) g_{ij}(1,2) \delta(r_{12} - \sigma_{ij}) (z_{12}/r_{12}) + \\ & + \int d\vec{r}_2 \sum_j q_j(2) h_{ij}(1,2) \nabla_1 (e_i e_j / \epsilon r_{12}) \end{aligned} \quad (15).$$

We assume first that the inhomogeneous pair correlation function is known. Then equations (11) and (15) form a closed pair of equations for the unknown $\phi(1)$ and $q_1(1)$. A computationally convenient form of these is obtained by noting that (11) is really the

Poisson equation

$$\nabla^2 \phi(1) = -4\pi / \epsilon \sum_i e_i \rho_i(1) \quad (16),$$

and that integrating (15) once, we obtain a modified Boltzmann equation

$$\ln(\rho_i(1)/\rho_i) = -(1/k_B T) (e_i \phi(1) + J_i^F(1) + e_i \phi_1^F(1)) \quad (17),$$

where the excluded volume term is

$$J_i^F(z) = -2\pi k_B T \sum_j \int_z^\infty dz_1 \int_{[0, z_1 - \sigma_{ij}]^{z_1 + \sigma_{ij}}} dz_2 z_{12} \rho_j(z_2) g_{ij}^+(\sigma_{12}, z_1, z_2) \quad (18),$$

where $g_{ij}^+(\sigma_{12})$ is the contact inhomogeneous pair correlation function and the fluctuation potential is

$$\phi_i^F(z) = -2\pi / \epsilon \sum_j e_j \int_z^\infty dz_1 \int_0^\infty dz_2 \rho_j(z_2) z_{12} \int d\vec{R}_{12} h_{ij}(1,2) / r_{ij}^3 \quad (19),$$

where $\vec{R}_{12} = (x_{12}, y_{12})$ is a vector in a plane perpendicular to z_{12} .

In our work we use the ansatz of ref. 13. For the restricted case of equal diameters $\sigma = \sigma_{ij} = \sigma_i = \sigma_j$ we have:

$$g_{ij}(1,2) = A(z_1, z_2) h_{ij}^{PY}(1,2) + f_i(1) f_j(2) h_{ij}^{bulk}(r_{12}) \quad (20),$$

where

$$\begin{aligned} A_{ij}(z_1, z_2) &= A_{ij} & \text{for } z_1, z_2 < 2\sigma_{ij} \\ &= 0 & \text{otherwise} \end{aligned} \quad (21)$$

and $h_{ij}^{PY}(r_{12})$ is the bulk Percus-Yevick pair correlation function.

In general, however, we have used $A_{ij} = A$

The functions $f_i(z)$ are found by requiring that the local electroneutrality is satisfied^(9,10)

$$-e_i = \sum_j e_j \int d\vec{r}_2 \rho_j(2) n_{ij}(1,2) \quad (22)$$

The effect of the first term in eq. (20) is to eliminate the region of negative $g_{ij}(1,2)$ which otherwise could occur in the neighbourhood of the electrode surface⁽¹⁰⁾.

Sect. III: Results.

The calculations were performed by the technique described elsewhere⁽¹⁰⁾, integrating the Poisson differential equation using a more refined version of the predictor-corrector integration routine than in ref. (10), which enhances significantly the convergence rate

Typically 3 to 5 iterations are needed for the lower densities. For higher molarities we need at most 10 iterations to reach convergence.

In our calculations we have used the same parameters as those in the Monte Carlo simulations of Torrie and Valleau⁽¹⁶⁾:

$\sigma = 4.25 \text{ \AA}$, $\epsilon = 78.4$, $T=298 \text{ K}$ The adimensional surface charge is $\sigma^* = q_s \sigma^2 / e$ where q_s is the surface charge density (usually in units $\mu\text{C}/\text{cm}^2$) The plasma parameter $\Gamma = \beta e^2 / \epsilon \sigma = 1.6809$ and $\beta = 1/k_B T$. Similarly, the adimensional potential drop is

$$\psi^* = \beta e \phi$$

where ϕ is the potential drop across the interface (usually in millivolts). We have explicitly, for the above parameters,

$$q_s = 88.7 \sigma^* (\mu\text{C}/\text{cm}^2) \quad \phi = 25.7 \psi^* (\text{mV})$$

a) 1-1 electrolytes.

We have computed the potential and density profiles for solutions ranging from 0.1M to 4M, and surface charge σ^* ranging from 0.1 to 0.7. The diffuse layer potential drop for all the reported cases is given in Table I where we also display the Monte Carlo results and those of competing theories. The most extensive results are those of the MPB5⁽⁸⁾ and the HNC/MSA⁽⁷⁾.

It is noteworthy to say that the MPB5 uses a Debye-Huckel like bulk correlation functions, while the good agreement shown by the HNC/MSA is obtained through the use of bulk correlation functions which are poorer than those used in the HNC/HNC which is not a very good theory (ref. 6, 1979).

In our work we use most accurate bulk correlation functions⁽¹⁹⁾ which are in good agreement with earlier reported work of Rasaiah and Friedman⁽²⁰⁾, for those cases that these last authors have studied.

Furthermore, our work will always satisfy the contact relation (1) within the numerical accuracy of the calculation, which is generally less than 1% in all cases investigated and typically close to 0.3%. This is particularly important for high densities and low couplings. Again, neither the MPB5 nor the HNC/MSA will satisfy this relation exactly. For the 0.1M the results are given for $\sigma^* = 0.1, 0.2$ and 0.3 : the potential drop ψ^* are not ^{as} accurate as those of the MPB5.

In figs.1-2 we show the potential and density profiles for the case $\sigma^* = 0.3$. The agreement of the BGY is better than that of the MGC, and in general quite good. We do not have data for this case from the MPB5. In the low density regime we experience numerical difficulties with the electroneutrality condition (22), which could be of technical nature.

The results are much better for 1.0 M solutions, in the sense that the overall agreement with the Monte Carlo is quite good. The BGY is slightly better than the HNC/MSA and slightly worse than the MPB5 for surface charges below $\sigma^* = 0.5$. For $\sigma^* = 0.55, 0.6$ the agreement to MC is good (see fig.3)

Recently Nielaba and Forstmann⁽²¹⁾ have reported a new approximation, the HNC/LMSA, where the correlation functions are computed using the MSA at a local average concentration. The results for the potential as a function of the reduced charge are shown in fig. 3, where it is also visible the failure of the HNC/MSA for high charge densities.

In fig. 4 we show a comparison of the case with $\sigma^* = 0.141$ (1-1 case at 1.0M) with MC results. The agreement is very good and of comparable accuracy than MPB4⁽¹⁶⁾.

For highest surface charge we show both the potential profile (fig. 5) and the charge profiles(fig.6). It is interesting to note that the BGY reproduces quite well the qualitative features of the counterion density profile, in particular the density oscillations near $z=1$. The agreement is however not as good as that of Nielaba and Forstmann⁽²¹⁾, but we do not have any adjustable parameter in our calculation.

This feature of density oscillation due to a layering near the electrode surface is also present in the higher density regime. For the 2.0M case, already investigated in ref .(13), the agreement in the potential drop is quantitative, while the density profiles are in remarkably good agreement with the MC results.

In fig. 7 we show the potential drop as a function of the surface charge for 2.0M and 3.0M . On the basis of these results we also are able to compute the differential capacitance of the dif-

fuse layer, a quantity of interest to the electrochemists.

In fig. 8 we show the potential and density profiles for 3.0 and 4.0 M solutions. These show very pronounced layering. The potential profile also shows a minimum which is deeper for the higher density case.

b) 2-2 electrolytes.

We have computed results for two concentrations: 0.05 M and 0.5 M. The results for the potential drop are displayed in Table II. Here again, the results for the more dilute case are not as good as those of the MPB5, while the 0.5M case is in excellent agreement. We experience also here severe problems with the electroneutrality relation, which could again be of^a technical nature.

The results for the potential drop are shown in fig. 9, where we also display the differential capacitance.

In fig. 10 we show the charge distribution of the 0.05M (2-2) case. In spite of the poor agreement of the potential drop, the density profile are in qualitative agreement with the MC results. The counterion profile is displaced to the right, and the coion profile has a peak at the correct place.

For the 0.5M case the results for the potential and density profiles are shown in figs. 11 and 12. The agreement here is good both in the potential drop and in the density profiles. In particular, the potential profile is in good agreement near the wall, but the BGY is higher than the MC far from the wall. The MPB5 is always lower than the MC result.

c) Asymmetric case.

Two concentrations were investigated: 0.05M and 0.5 M for the

2-1 and 1-2 cases. The results for the potential drop are displayed in table III. Again, here the agreement for the more dilute case is poorer, presumably due to technical reasons.

Fig. 13 shows the results of the potential drop, as well as those of the differential capacitance, for the asymmetric case. As can be seen the agreement is better for singly charged counterions. Figs. 14 and 15 show the potential and density profiles for the 0.5M (1-2, i.e. doubly charged counterion) at surface charge $\sigma^* = 0.1704$. While the potential profile is very similar to that of the MPB5, the density profiles are slightly better and in excellent agreement with the MC profile.

We have also performed the calculation of the $\sigma^* = 0, 0.5$ M case, recently reported by Torrie, Valleau and Outhwaite⁽¹⁶⁾. Fig. 16 shows the potential profile, which is slightly inferior to the MPB5 result, and fig. 17 the density profiles, which are slightly better than the MPB5

Concluding remarks.

In the present work we have presented an extensive discussion of the use of the BGY for charged interfaces. The BGY equation is an exact relation but requires a closure, which is an ansatz for the inhomogeneous pair distribution function $g_{ij}^{(1,2)}$.

In this work we have used a construct⁽¹³⁾ that removes some of the unphysical regions with negative $g_{ij}^{(1,2)}$ that occurred when the modified superposition ansatz^(9,10) was used. The results are in very good agreement for high salt concentrations but definitely poorer for dilute solutions. The addition of a repulsive part to the pair interaction near the wall takes into account higher repulsive interactions due to a crowding effect. We must remark that the

effect of this term is in general not very large. However, it increases very significantly the stability of the iteration procedure.

The poor performance for dilute solutions is attributed to difficulties with the electroneutrality rule, which could also be of a technical nature. We will investigate this point in the future.

The main objective of our work is to find an equation that will perform well in the high density-high coupling regime which is that of the molecular solutions or molten salts near a metal electrode. Our equation is indeed well behaved in this regime, and we have been able to obtain physically reasonable solutions at 3.0 M and 4.0 M, for fairly high surface charges.

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Table I (a)

σ^*	M^*	MG^*	MPRG	HPG / MSA	RGY	n° iter.	Contact (b)	Contact RGY
1-1 Electrolyte 0.1M								
0.1	2.88	3.17	2.88		3.03	2	24.73	24.74
0.2	4.02	4.54	4.02		4.26	2	93.27	93.26
0.3	4.63	5.34	4.70		5.00	2	207.50	207.80
1-1 Electrolyte 1.0M								
0.1	1.09	1.4	1.00	0.985	1.055	4	4.47	4.47
0.141	1.47	1.85	1.4		1.437	4	6.73	6.73
0.25	2.13	2.79	2.13	1.95	2.31	4	16.47	16.50
0.425	3.08	3.74	3.00	2.44	3.46	5	43.43	43.66
0.55	4.15	4.26	—		4.21	5	71.3	71.89
0.6	4.38	4.43	—		4.48	5	84.43	85.21
0.7	5.71	4.74	—		5.02	5	114.13	115.55
1-1 Electrolyte 2.0M								
0.396	2.29	2.99	—		2.303	9	20.70	20.75

Table II

σ^*	MP	MGC	MPB5	HNC / MSA	BGY	n° iter.	Contact	Contact BGY
				2-2 Electrolyte 0.05M				
0.2	1.33		1.33	-1.4	1.81	4	184.09	186.2
0.284	1.14		1.30	-1.08	1.91	4	369.86	376.7
				2-2 Electrolyte 0.5M				
0.1704	0.67	1.362	0.5	0.5	0.638	4	14.48	14.68

Table III

σ^*	M ⁺	MG ⁺	MPBS	HNC/MSA	BGY	n° iter.	Contact	Contact BGY
				2-1 Electrolyte 0.05M				
0.0929	1.73		1.70		1.705	3	7.319	7.325
0.18	3.99				4.04	2	100.39	100.5
				1-2 Electrolyte 0.05M				
0.05	1.05		1.05		1.11	3	9.318	9.339
0.0975	1.21		1.21		1.476	3	30.66	30.76
0.126	1.26		1.27		1.597	3	50.06	50.28
0.2	1.18		1.27		1.739	4	123.55	124.87
0.284	1.02		1.27		1.74	4	247.39	251.79
				2-1 Electrolyte 0.5M				
0.0989	1.04	1.310	0.986	1.004	0.97	4	4.78	4.78
0.2	1.94	2.365	1.85	1.898	1.875	4	13.99	14.03
				1-2 Electrolyte 0.5M				
0.05	0.4		0.373	0.336	0.372	3	2.576	2.571
0.099	0.5		0.463	0.471	0.509	4	4.7	4.816
0.1704	0.45		0.460	0.487	0.574	5	10.65	10.787
0.24	0.35		0.411	0.354	0.557	5	19.35	19.73

Table Captions

Table I: (a) Diffuse layer potential drop $\psi^*(0)$ for 1-1 electrolytes. MC results :G.M.Torrie and J.P.Valleau (1980), (ref. 16);MPB5:C.W.Outhwaite and L.B.Bhuiyan (1983),(ref. 8);HNC/MSA:M.Lozada-Cassou et al. (1982),(ref. 7)
(b) As calculated from the r.h.s. of eq. (1).

Table II:Diffuse layer potential drop $\psi^*(0)$ for 2-2 electrolytes. MC results:G M.Torrie and J.P.Valleau (1982),(ref. 16); MPB5 and HNC/MSA same captions as Table I. The HNC/MSA results at 0.05 M have been taken from a graph.

Table III: Diffuse layer potential drop $\psi^*(0)$ for 1-2 and 2-1 electrolytes. Same captions as Table II.

- Fig. 1 : Potential profile for a 1-1 electrolyte at $c=0.1M$ and $\sigma^*=0.3$. Dots, MC results(ref.16); full line, this work.
- Fig. 2 : Density profiles for the case of fig. 1. Dots and crosses, MC results;full line, this work.
- Fig. 3 : Diffuse layer potential drop $\psi^*(0)$ ($\sigma/2$ is taken as coordinate origin) as a function of the surface charge density σ^* . Dots, MC;dashed line, HNC, LMSA;dashed-double dot line,MPB5;dash-dot line,HNC,MSA; full line, this work. Also shown is the differential capacitance in the BGY(this work), whose scale is on the right(in $8.854 \mu F/cm^2$ units).
- Fig. 4 : Density profiles for the 1-1 electrolyte at $c=1.0M$ and $\sigma^*=0.141$. Dots and crosses,MC results;full line, dashed line, this work.
- Fig. 5 : Same captions as fig. 1 except that $C=1.0M$ and $\sigma^*=0.7$.
- Fig. 6 : Density profiles for fig. 5 case. Dots and triangles, MC results;open circles and crosses,HNC/LMSA; full line, dashed line, this work.
- Fig. 7 : $\psi^*(0)$ vs. σ^* for the 1-1 case at $c=2.0M$ and $3.0M$.BGY results:full line, $2.0M$;dashed line, $3.0 M$. Also shown are the differential capacitances(same units as fig 3).
- Fig. 8 : Potential and density profiles for 3.0 and $4.0M$ concentration of the 1-1 electrolyte. From top to bottom: potential, counterion, coion profile. Dash-dot line, $3.0M$ at $\sigma^*=0.485$.Full line, $3.0M$ at $\sigma^*=0.396$;dashed line, $4.0 M$ at $\sigma^*=0.56$.
- Fig. 9 : $\psi^*(0)$ and diff. capac. vs. σ^* for the 2-2 electrolyte at $c=0.5M$. (in the same units of fig.3)

- Fig. 10 : Density profiles for the 1-1 case at $c=0.5M$ and $\sigma^*=0.284$. Dots and crosses, MC results. Full line, this work; dashed line, Modified Gouy-Chapman.
- Fig. 11 : Potential profile for the 2-2 case at $c=0.5M$ and $\sigma^*=0.1704$. Dots, MC results; full line, this work; dashed line, MPB5.
- Fig. 12 : Density profiles for the case of fig. 11. Dots and crosses, MC results; the rest, same captions.
- Fig. 13 : $\psi^*(0)$ vs. σ^* for 1-2,2-1 electrolytes at different molalities. Counterion single charged for $\sigma^* > 0$, doubly charged for $\sigma^* < 0$. Concentration $c=0.5M$: dots, MC results; full line, this work. $c=0.05M$: crosses, MC results; dashed line, this work. Dash-dot line: differential capacitance for the $c=0.05M$ case (same units of fig 3).
- Fig. 14 : Potential profile for the 1-2 (doubly charged counterion) case at $c=0.5M$ and $\sigma^*=0.1704$. Dots, MC results; dashed line MPB5; full line, this work.
- Fig. 15 : Density profiles for the case of fig. 14. Dots and crosses, MC results. For the rest same captions.
- Fig. 16 : Potential profile for the 1-2 case at $\sigma^*=0$ and $c=0.5M$. Dots, MC results; crosses, MPB5; full line, this work.
- Fig. 17 : Density profiles for the case of fig. 16. Single charged ion: crosses, MC results; dash-double dot line, MPB5; dashed line, this work. Doubly charged ion: dots, MC results; dash-dot line, MPB5; full line, this work.

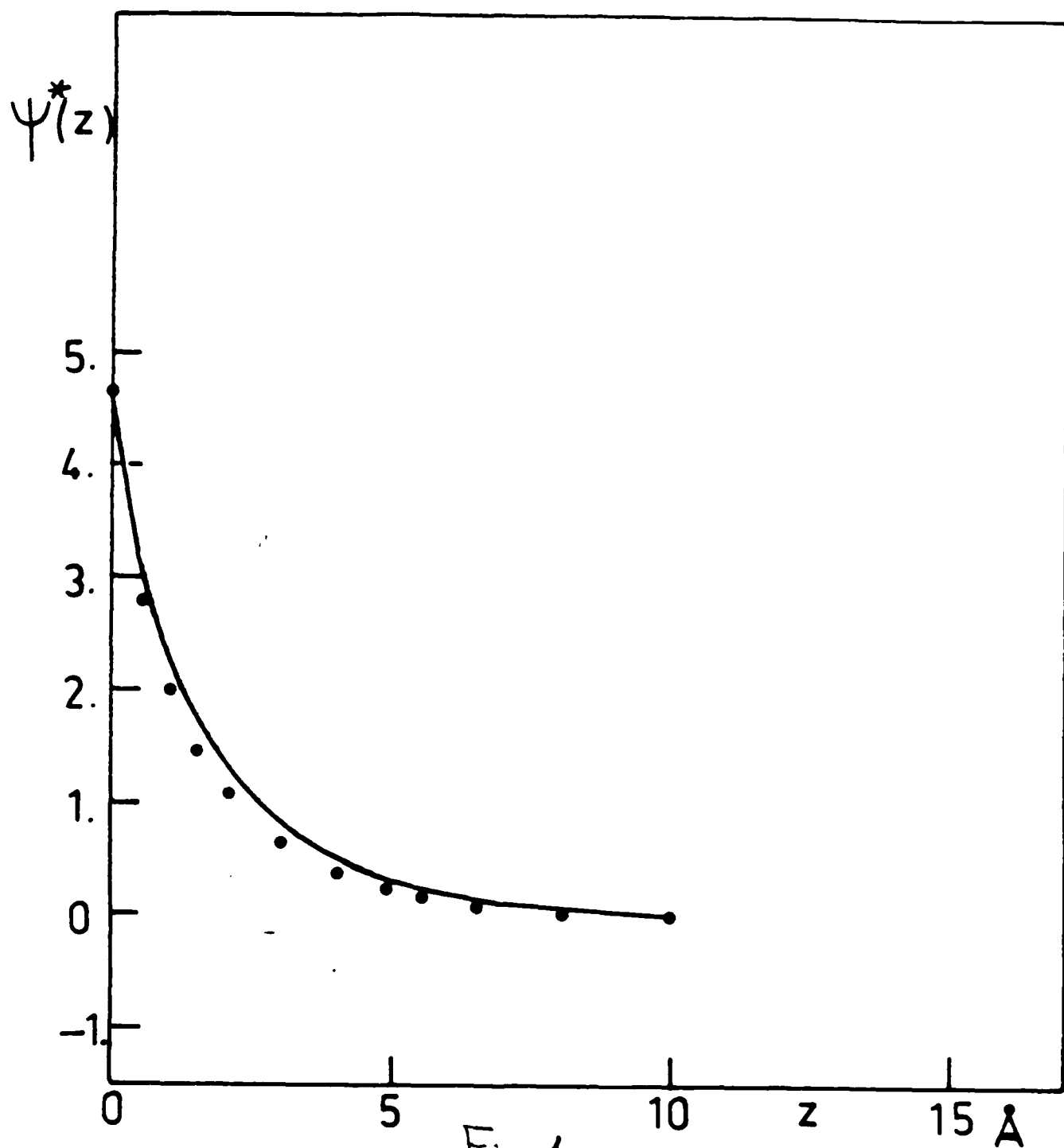


Fig. 1

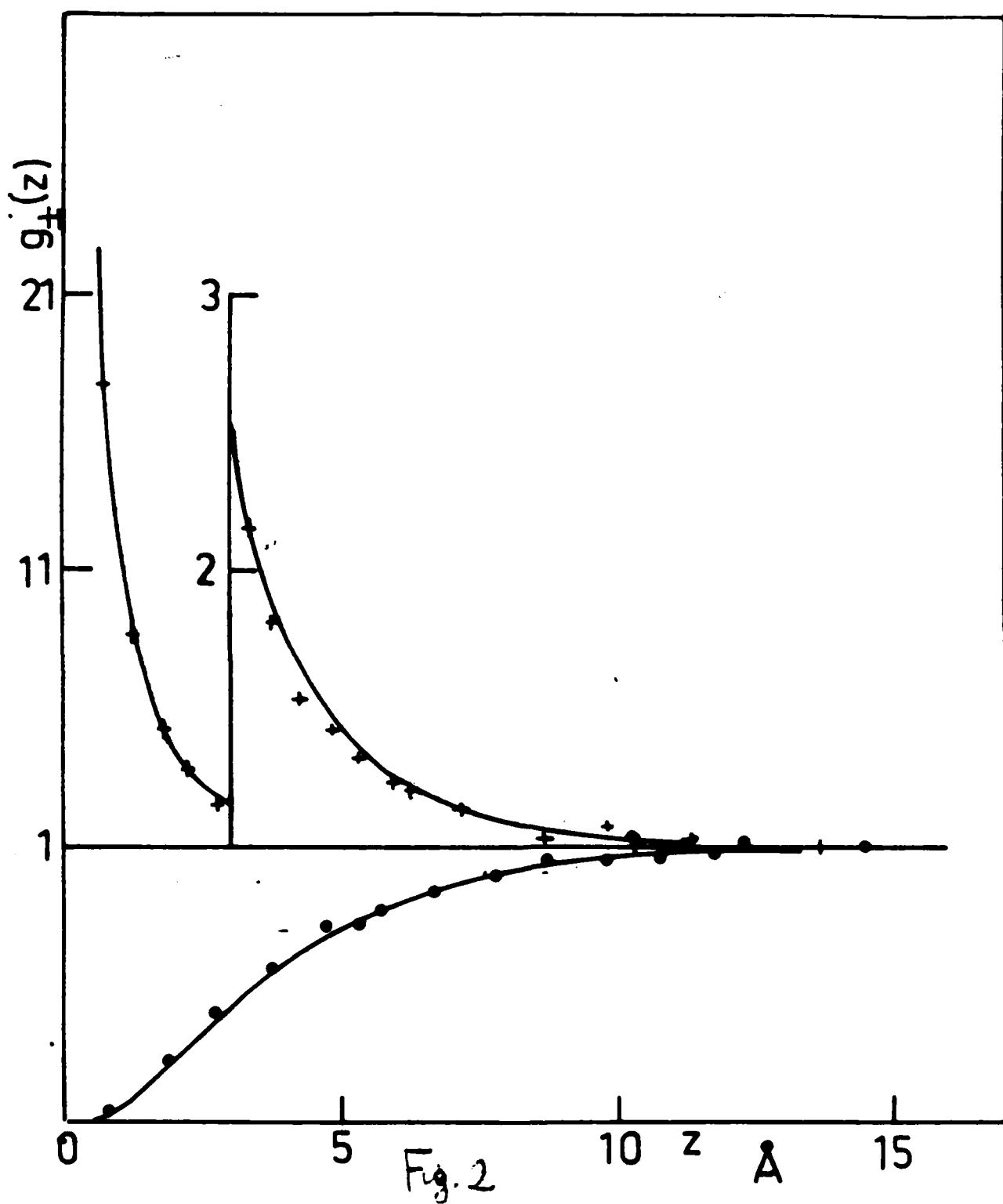


Fig. 2

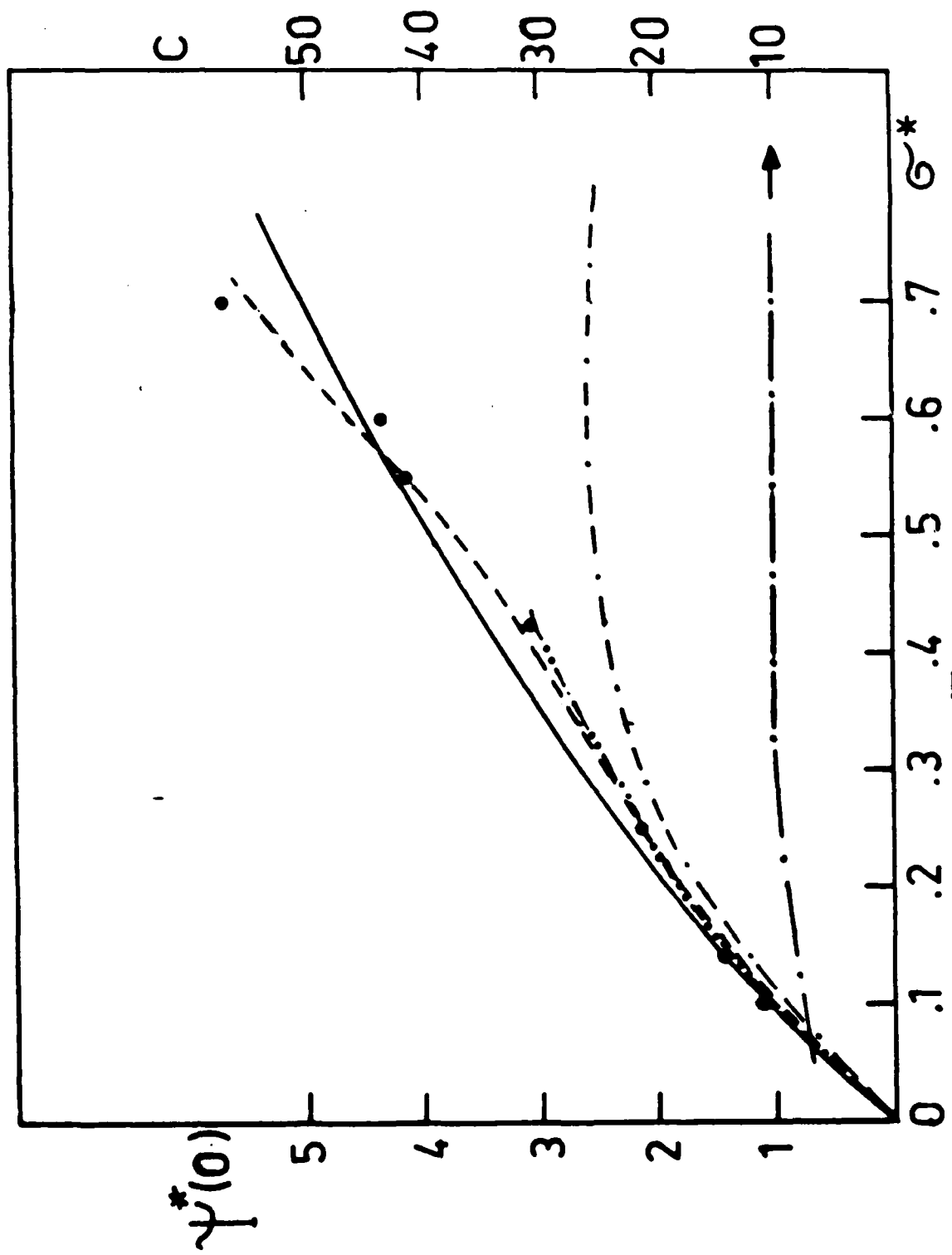
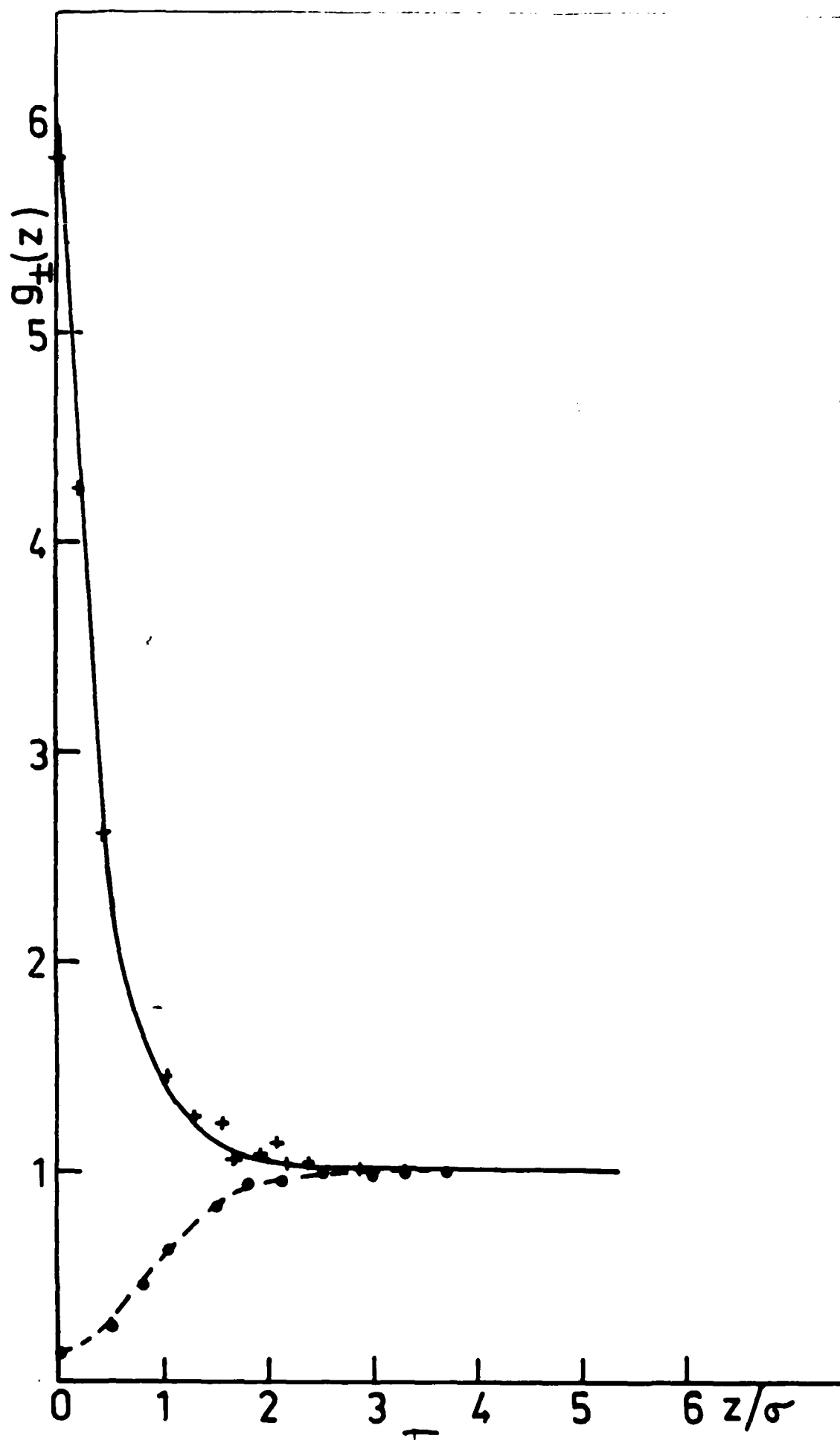


Fig. 3



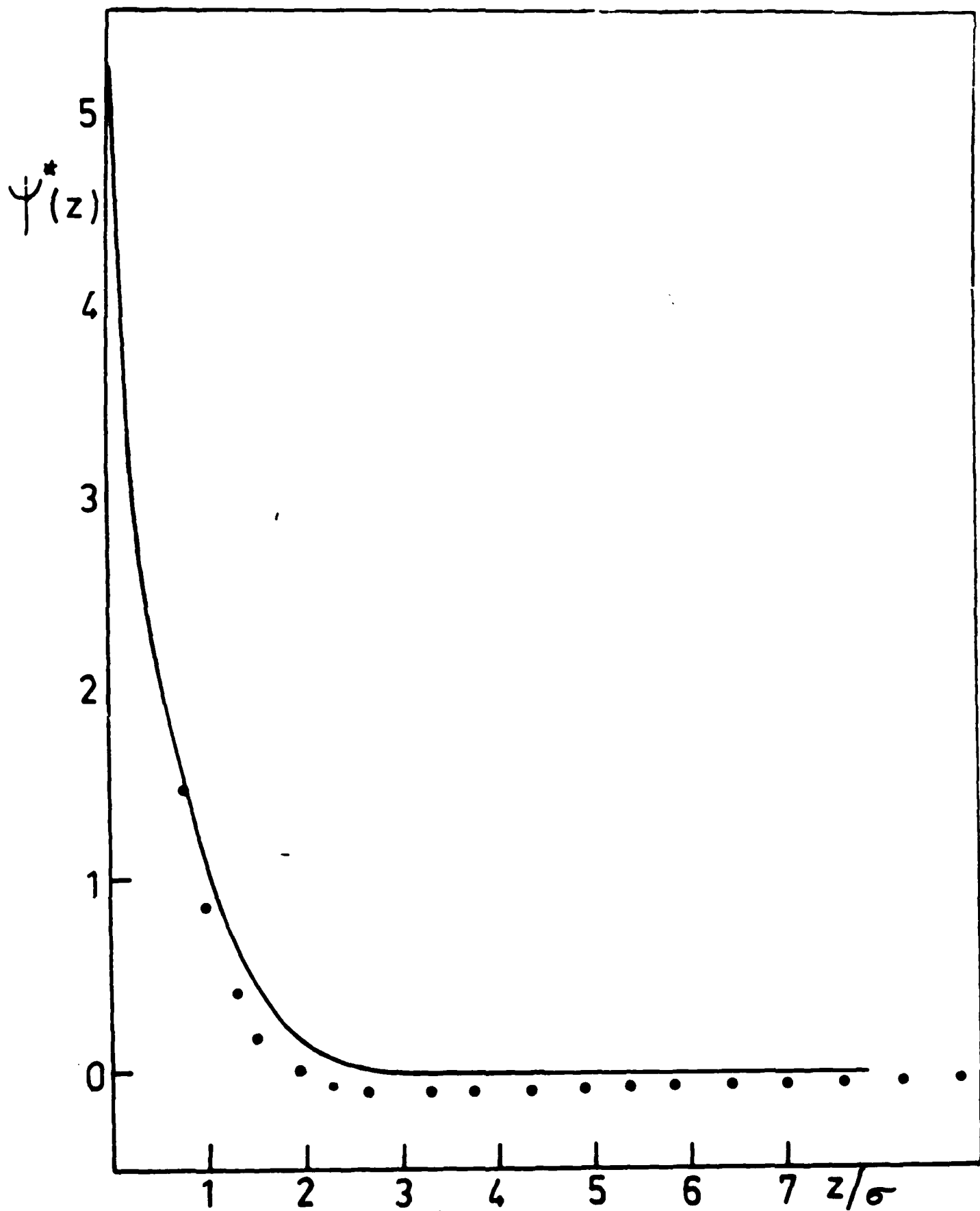
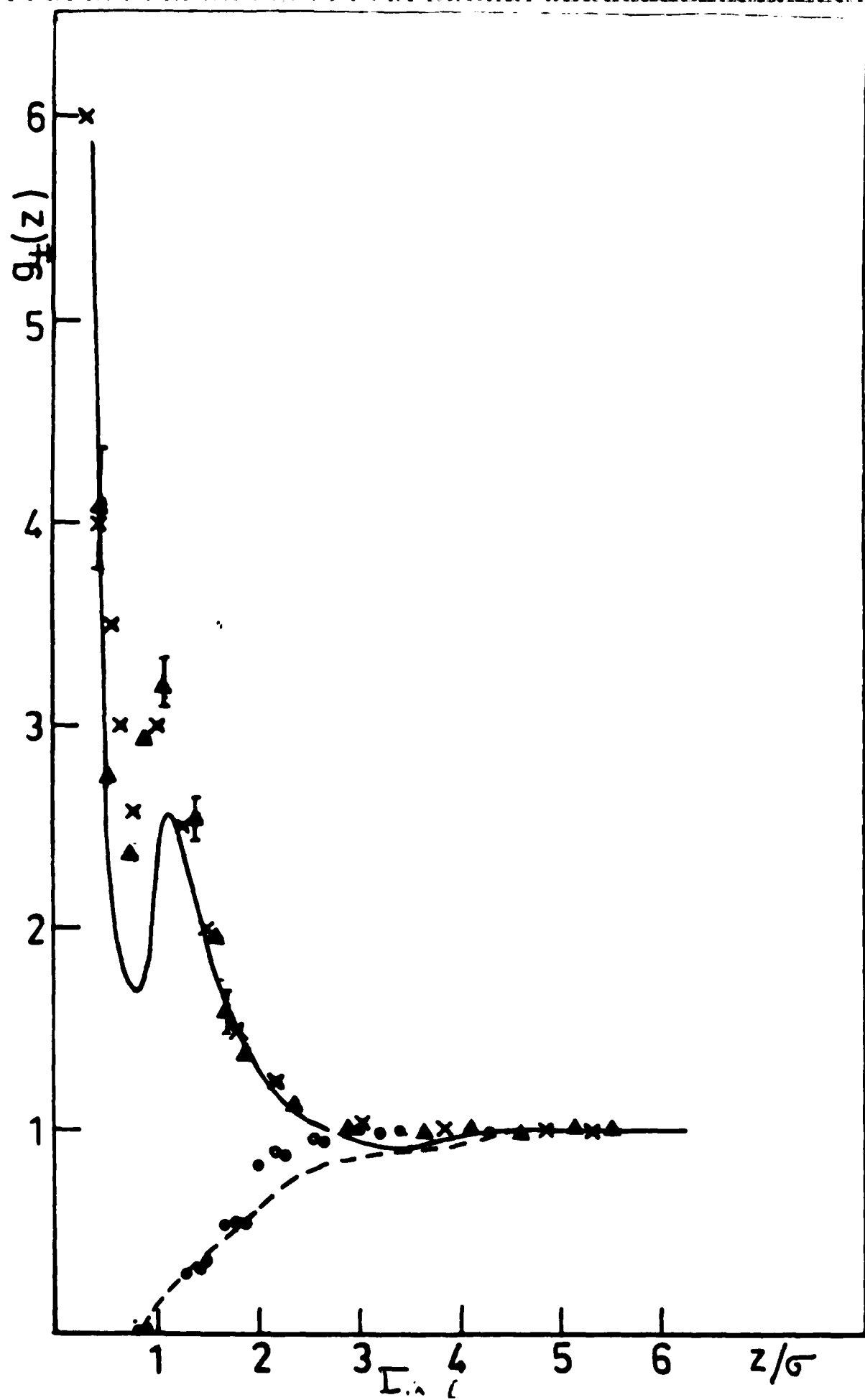


Fig 5



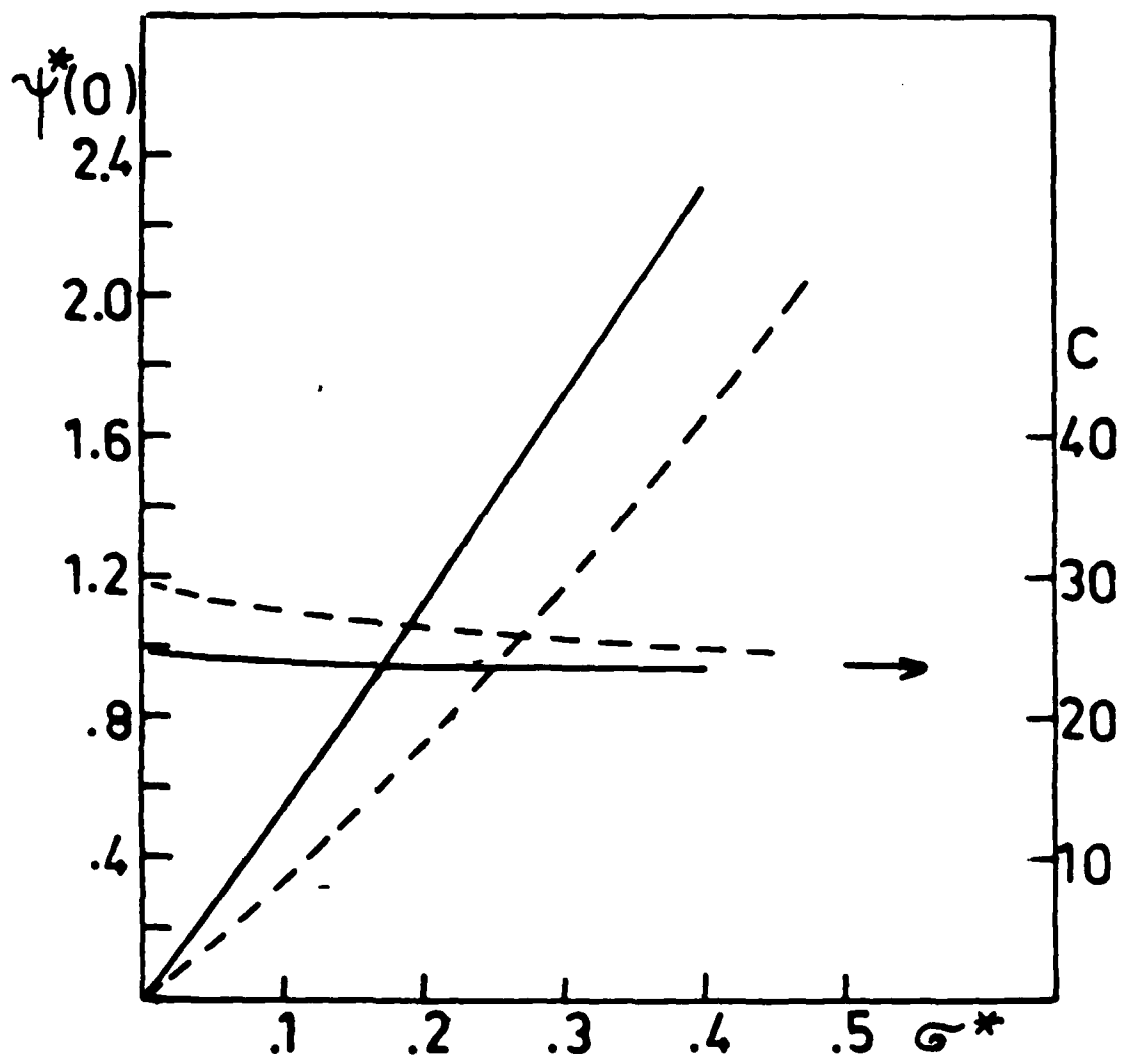
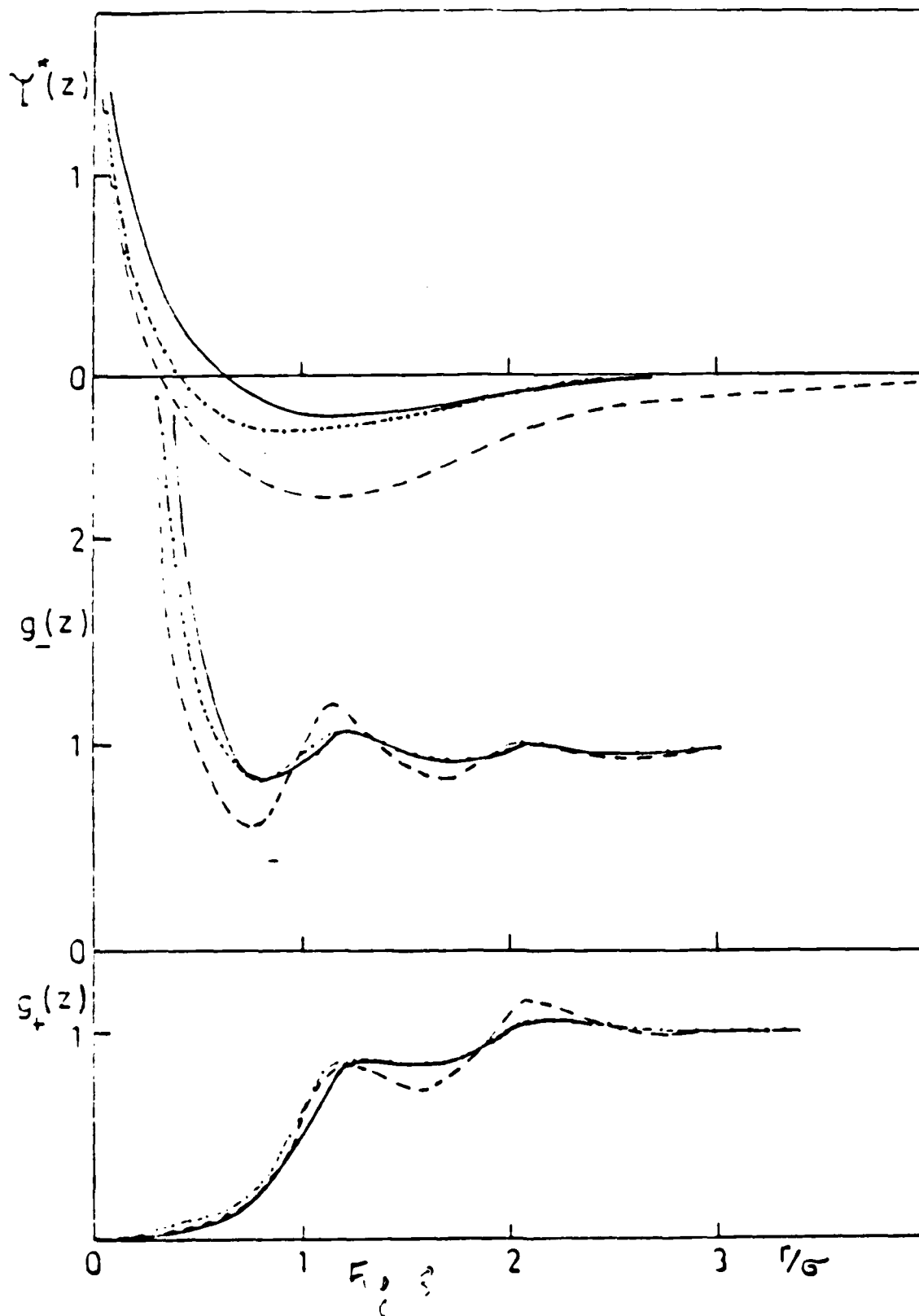


Fig. 7



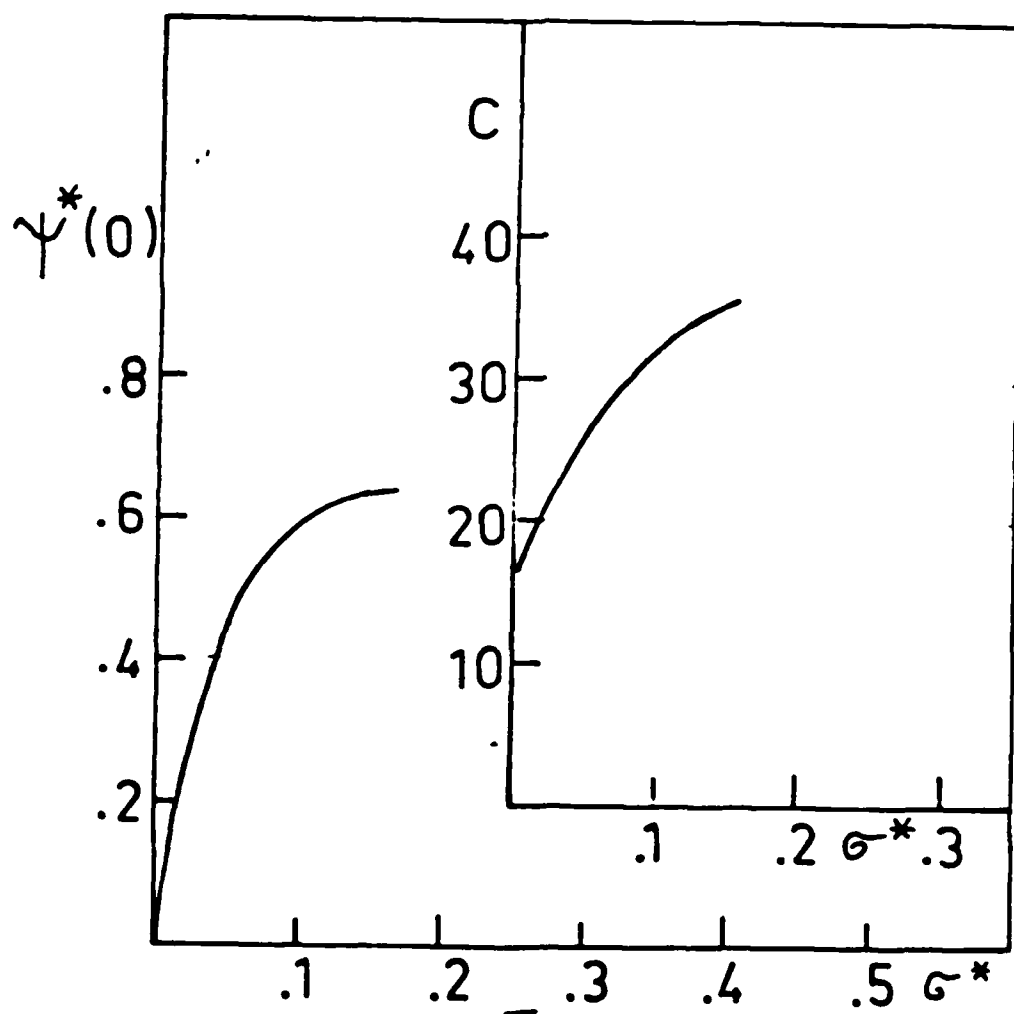


Fig. 2

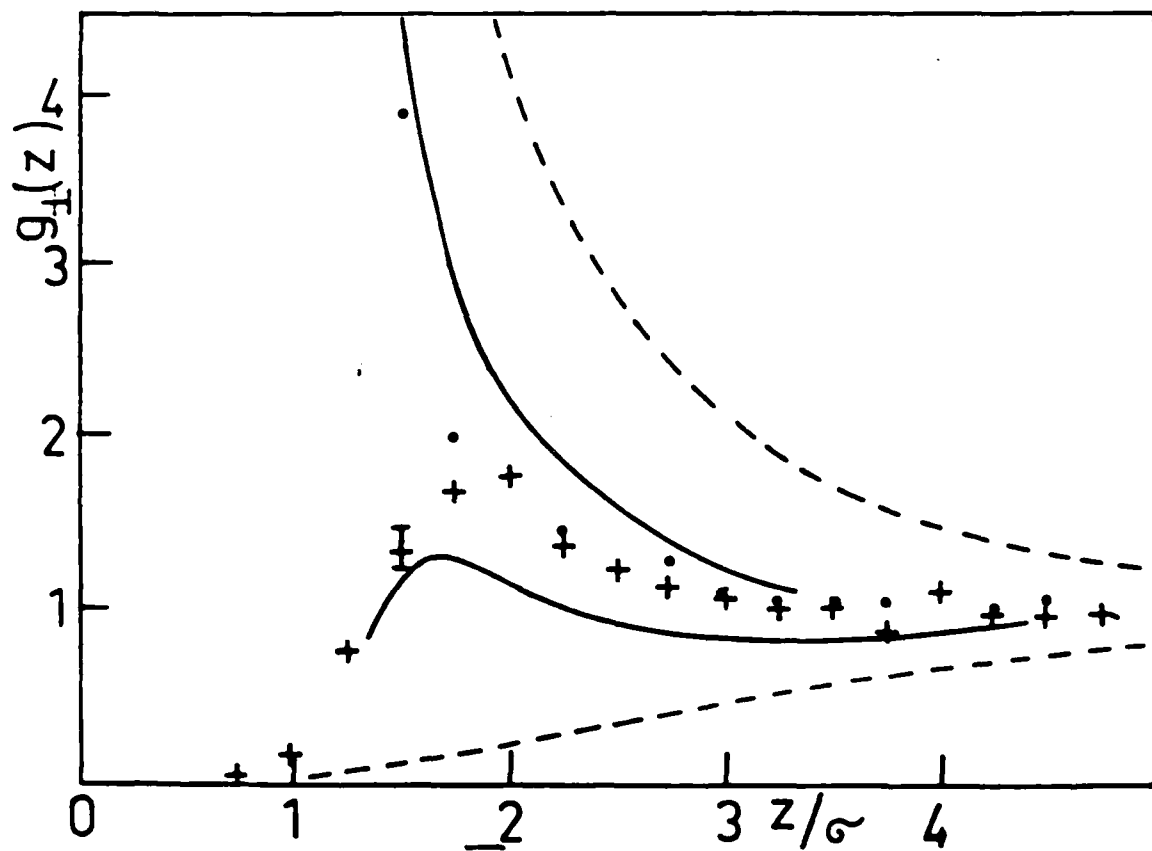


Fig. 10

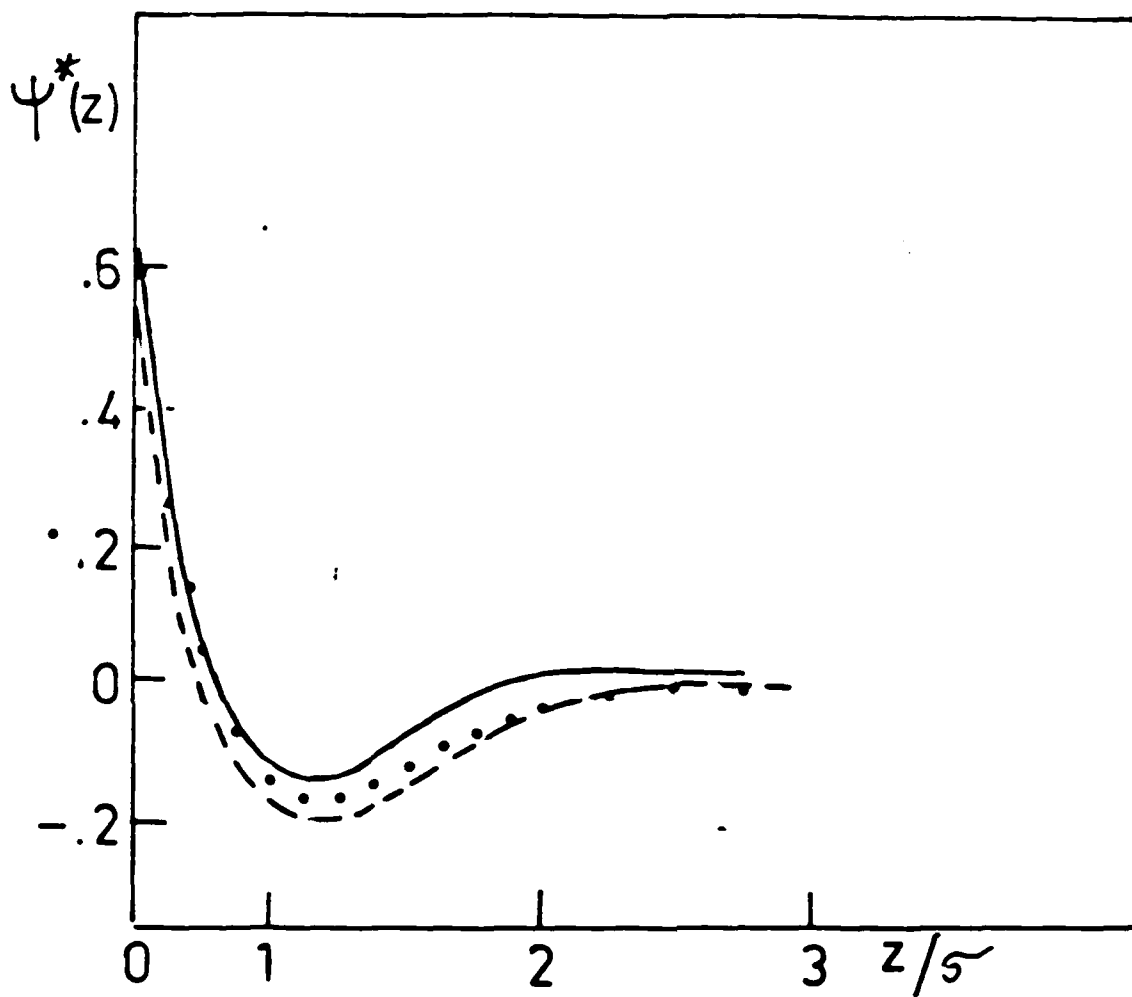


Fig. 11

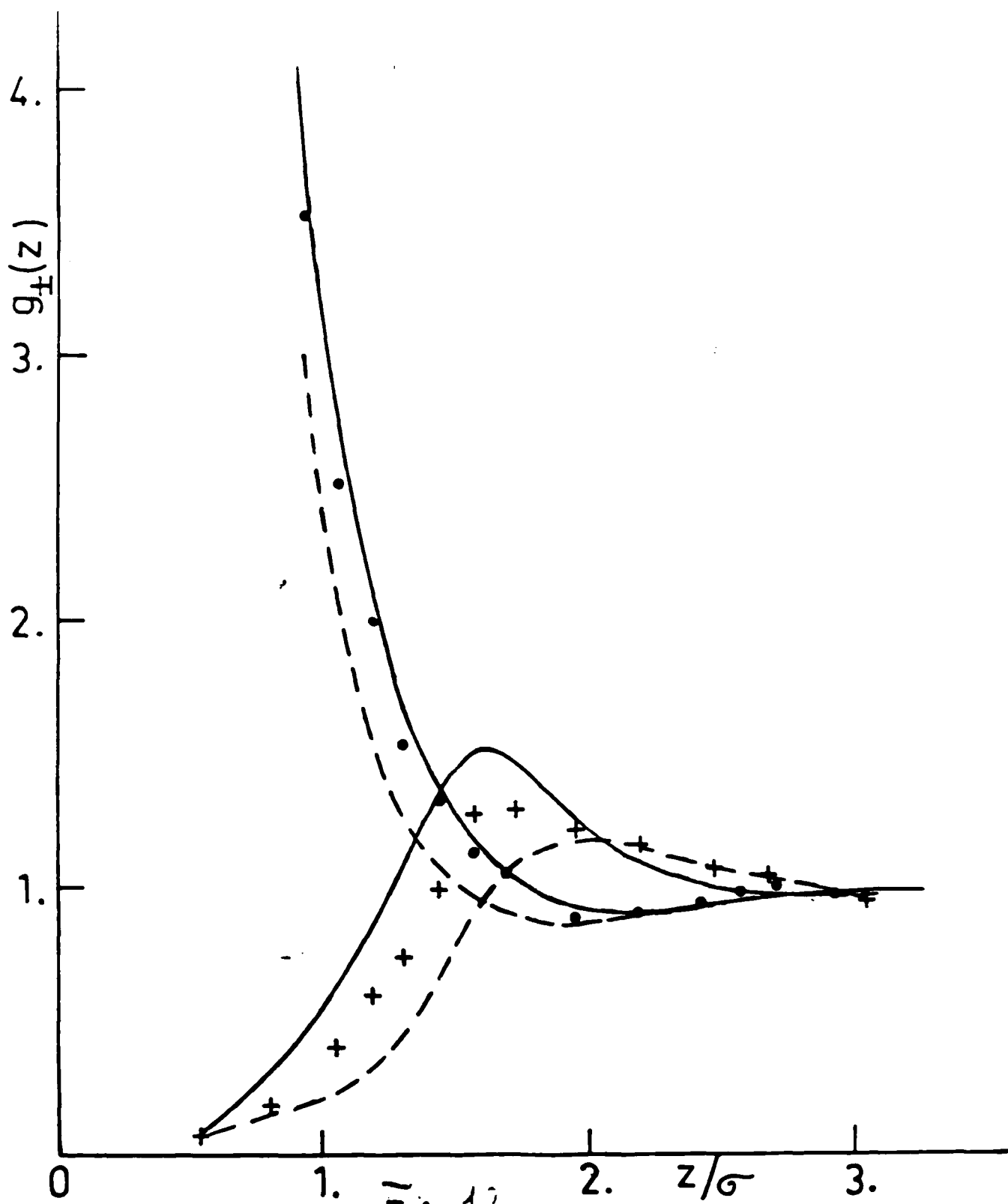


Fig. 12

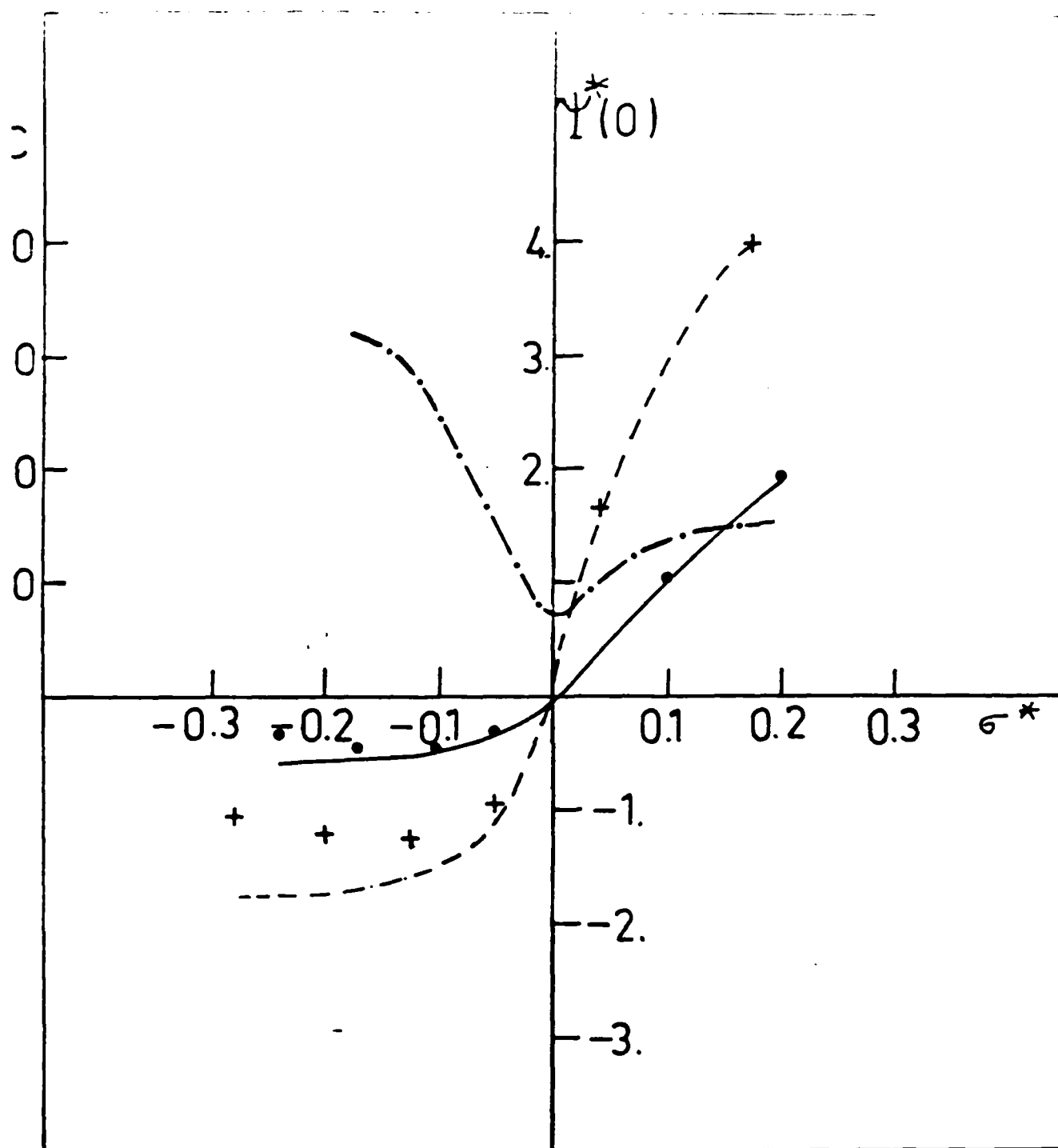


Fig. 13

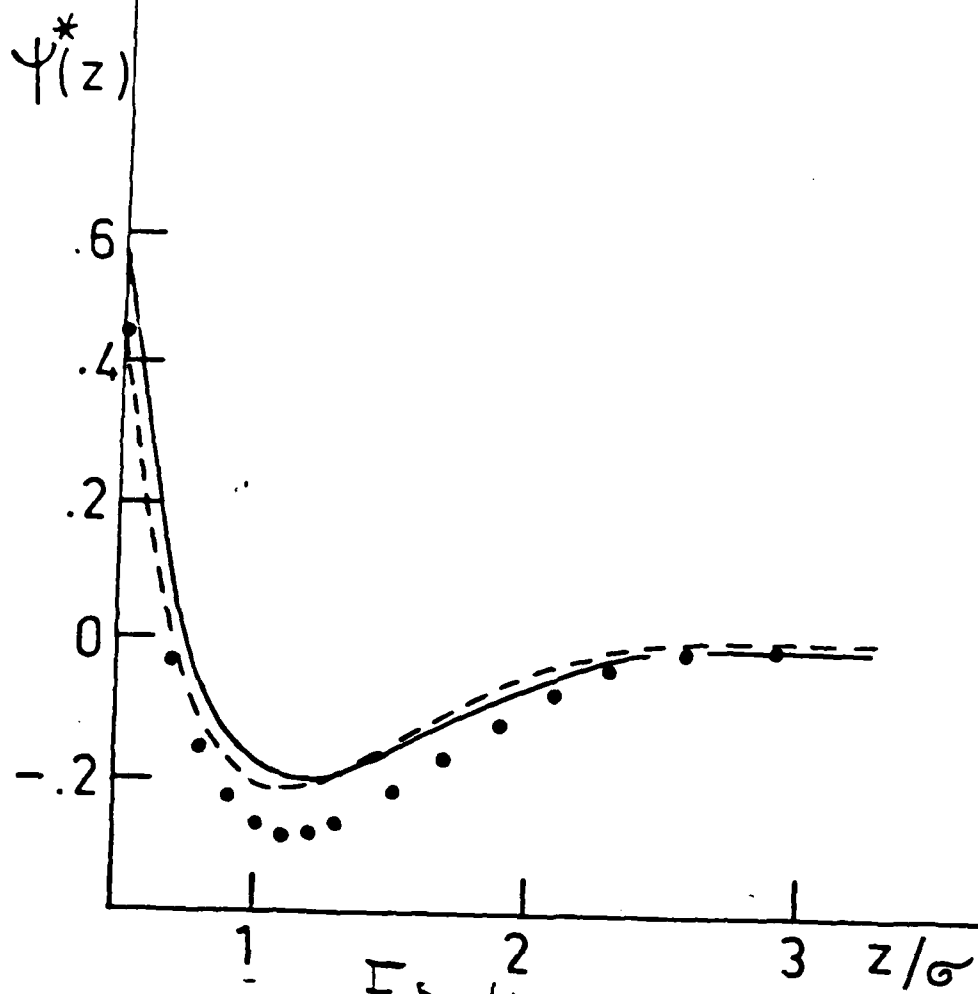
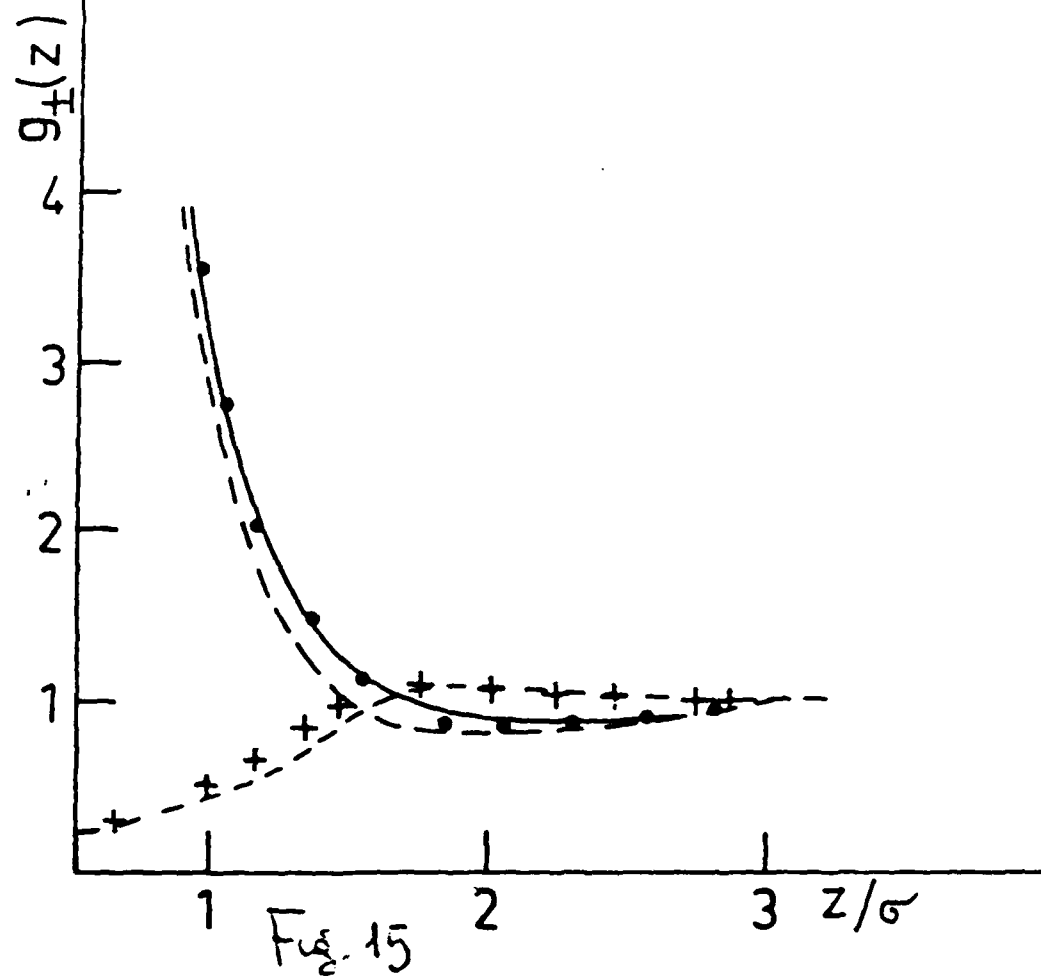


Fig. 14



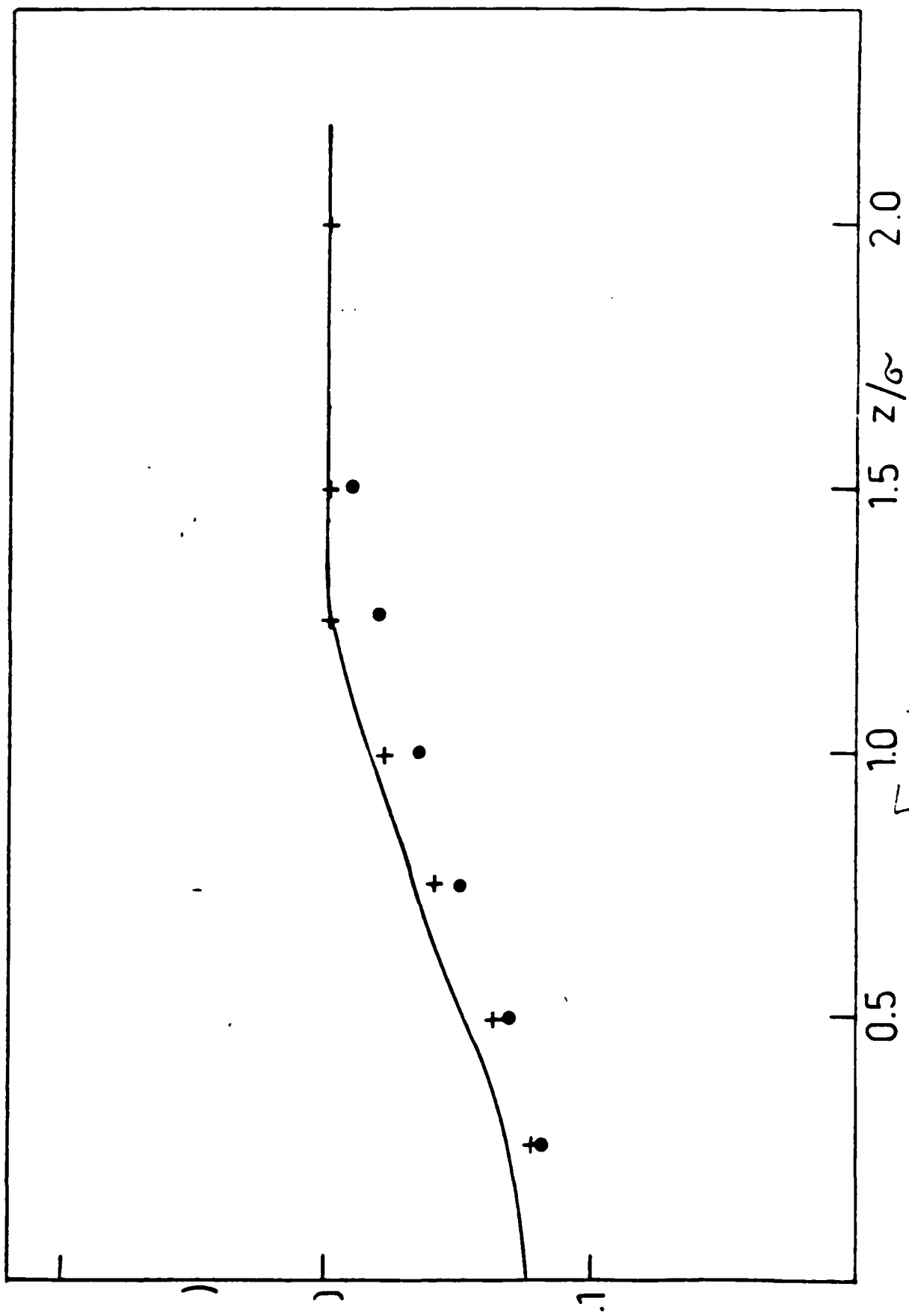
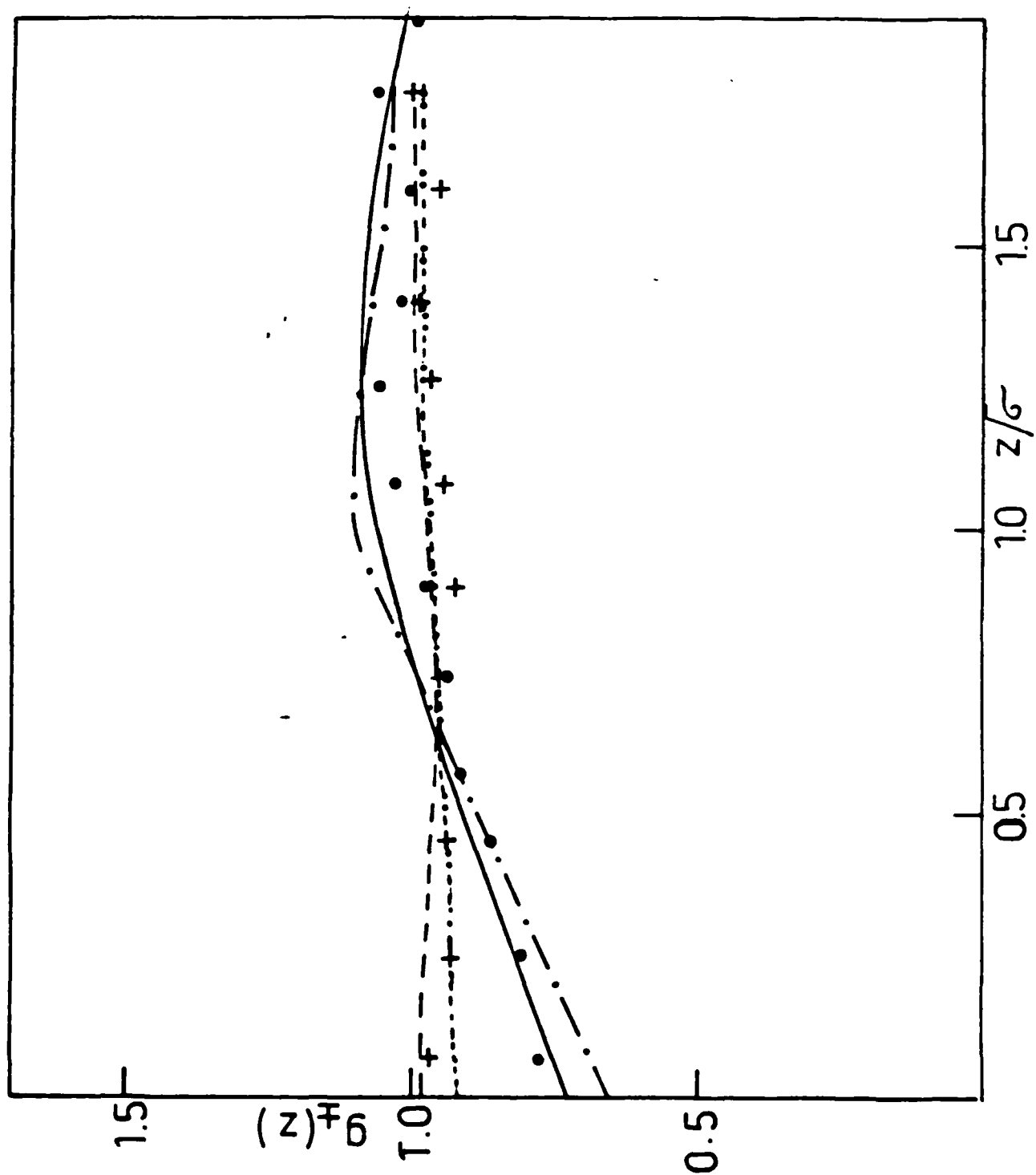


Fig. 16.



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